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Structure of the Ion-Pair Charge-Transfer Complex (Methylviologen)$^{2+}$[Pd(mnt)$_2$]$^{2-}$

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Abstract

The structure of the ion-pair charge-transfer complex *N,N'*-dimethyl-4,4'-bipyridinium bis(*cis*-1,2-dicyanoethene-1,2-dithiolato)palladate(II), MV[Pd(mnt)$_2$], consists of columns of alternating planar methylviologen dications and planar dithiolene palladate dianions along the *a* axis. The shortest intrastack and interstack distances of 3.42 and 3.34 Å, respectively, are in the range of van der Waals contacts. The compound is isomorphous with the corresponding Ni homologue.

Comment

In recent years we have been investigating ion-pair charge-transfer (IPCT) complexes of dianionic transition-metal dithiolenes with the methylviologen dication MV^{2+} and related bipyridinium acceptors. These compounds are of particular interest since they show photoinduced electron transfer from the dithiolene to the bipyridinium component, which might qualify them as photosensitizers for the photoreduction of water with visible light. In the solid state these composite materials are semiconductors and their electrical conductivities can be quantitatively tuned by variation of the redox potentials of the ions (Kisch *et al.*, 1991). In the diffuse reflectance spectra of the solid platinum-group complexes MV[M(mnt)$_2$] (mnt = *cis*-1,2-dicyanoethene-1,2-dithiolate), the IPCT band shifts from 920 to 785 and 905 nm when nickel is replaced by palladium and platinum, respectively. This reflects the different reducing powers of [M(mnt)$_2$]$^{2-}$ (McCleverty, 1968). In the following, we report on the crystal and molecular structure of MV[Pd(mnt)$_2$].

The coordination geometry of the hitherto structurally uncharacterized [Pd(mnt)$_2$]$^{2-}$ dianion is square planar but the cyano groups C3≡N1 are markedly bent out of the mean plane containing Pd, S1, S2, C1 and C2 by 0.38 (N1) and 0.21 Å (C3) (Fig. 1). As similar distortions are found in the structures of (NBu$_4$)$_2$[Ni(mnt)$_2$] (Kobayashi & Yukiyoshi, 1977) and MV[Ni(mnt)$_2$] (Kisch, Fernandez, Wakatsuki & Yamazaki, 1985) they should be assigned to crystal packing effects. The significant bond lengths and bond angles of [Pd(mnt)$_2$]$^{2-}$ given in Table 2 compare well with the data reported for the mono-anionic [Pd(mnt)$_2$]$^-$ in the case of [perylene]$_2$[Pd(mnt)$_2$] (Domingos *et al.*, 1988). Relative to the monoanion, the Pd—S and C—S bonds of the dianion are elongated, in their arithmetic mean, from 2.26 to 2.30 and from 1.71 to 1.73 Å, respectively, as expected by molecular orbital theory (Schrauzer, 1968). The C1=C2 bond is almost unchanged according to values of 1.39 and 1.38 Å, respectively. The aromatic core of the bipyridinium component is planar and the bond lengths and angles agree well with those reported for MV[Ni(mnt)$_2$], and the methylviologen dihalides (Russell & Wallwork, 1972).

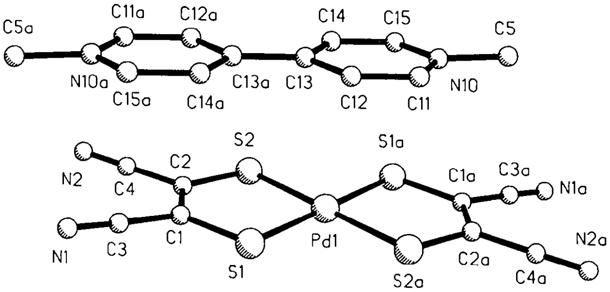

Fig. 1. Molecular geometry of MV[Pd(mnt)$_2$].

The compound crystallizes in space group $P\bar{1}$. The structure consists of mixed columns containing alternating palladium dithiolene and methylviologen components if viewed along the *a* axis (Fig. 2). The two components of the ion pair are arranged almost parallel with an angle of 5° between the perpendiculars of the their least-squares planes.

The shortest interionic distances within a stack are observed between C2—C12*a* (3.42 Å) and S1*a*—C15

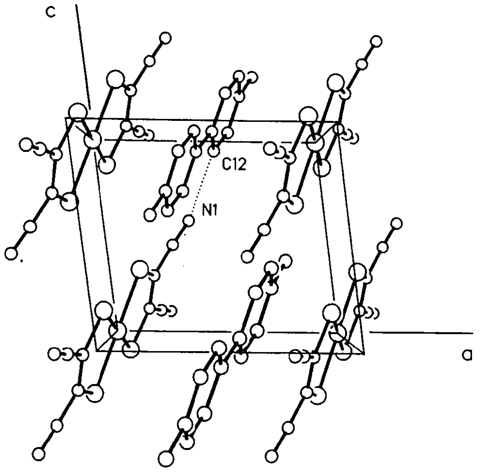

Fig. 2. View of the structure along the *b* axis.

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(3.47 Å) with the latter distance being slightly shorter than the van der Waals contact distances of 3.40 and 3.50 Å, respectively (Bondi, 1964). These distances agree very well with the corresponding value of 3.42 Å reported for MV[Ni(mnt)$_2$] and a methylviologen eosin complex (Willner, Eichen, Rabinovitz, Hoffman & Cohen, 1992).

The shortest interstack contacts are observed along the *c* axis and occur between N1 and the adjacent C12 (3.34 Å, Fig. 2), the corresponding van der Waals distance being 3.25 Å (Bondi, 1964). Calculated interstack-distances are shortest between thiolate S atoms and methylviologen H atoms (S1*a*—H14, 2.85 Å). Although within the limit for a hydrogen bond (3.0 Å; Bondi, 1964) these contacts should be assigned to packing effects because the angle C14—H14—S1*a* is only 128° and H14 is an aromatic atom.

Comparison of the structures of MV[Pd(mnt)$_2$] and MV[Ni(mnt)$_2$] reveals that in both complexes the shortest contacts involve the electron-rich S atoms (Clemenson, 1990) and the *ortho* (C15) viologen C atoms which are known to carry the highest positive charges (Burdon, Hayes & Pick, 1977; Hofmann, Cimiraglia & Tomasi, 1986). Although charge-transfer interaction in the case of the palladium complex should be weaker as indicated by the higher energy of the IPCT band, no significant differences are observed in the Ni complex in the solid-state structures. This suggests that the electrostatic interactions largely determine the relative arrangement of the donor-acceptor ion pairs.

Experimental

Crystal data

$[C_{12}H_{14}N_2][Pd(C_4N_2S_2)_2]$
$M_r = 573.03$
Triclinic
$P\bar{1}$
$a = 7.659$ (2) Å
$b = 11.158$ (2) Å
$c = 6.559$ (2) Å
$\alpha = 96.58$ (2)°
$\beta = 98.18$ (3)°
$\gamma = 87.80$ (2)°
$V = 551.0$ (3) Å^3
$Z = 1$
$D_x = 1.73$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 17.36$-20.41°
$\mu = 1.242$ mm^{-1}
$T = 293$ K
Rhombohedral
0.3 × 0.2 × 0.1 mm
Black
Crystal source: diffusion of methanol into a solution of the title compound in dimethyl sulfoxide

Data collection

Siemens *P*4 diffractometer
ω scans
3796 measured reflections
2417 independent reflections
2102 observed reflections [$F > 4.0\sigma(F)$]
$R_{int} = 0.0698$
$\theta_{max} = 27$°

$h = -9 \rightarrow 9$
$k = -14 \rightarrow 0$
$l = -8 \rightarrow 8$
3 standard reflections monitored every 100 reflections intensity variation: within statistical fluctuation

Refinement

Refinement on F
Final $R = 0.0253$
$wR = 0.0294$
$S = 1.77$
2102 reflections
143 parameters
H atoms not refined (riding model calculation)

Calculated weights $w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Atomic scattering factors from Siemens *SHELXTL-Plus* (VMS) (Sheldrick, 1991)

Data collection: Siemens *P3/V* data collection system. Cell refinement: Siemens *P3/V* data collection system. Data reduction: Siemens *SHELXTL-Plus* (VMS) *XDISK*. Program(s) used to solve structure: Siemens *SHELXTL-Plus* (VMS) *XS*. Program(s) used to refine structure: Siemens *SHELXTL-Plus* (VMS) *XLS*. Molecular graphics: Siemens *SHELXTL-Plus* (VMS) *XP*. Software used to prepare material for publication: Siemens *SHELXTL-Plus* (VMS) *XPUB*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd1	0.0000	0.0000	0.0000	0.0311 (2)
S1	0.1319 (1)	0.0736 (1)	0.3232 (2)	0.0416 (5)
S2	0.0331 (1)	0.1835 (1)	−0.1178 (2)	0.0418 (5)
C1	0.1865 (4)	0.2179 (3)	0.2859 (6)	0.035 (2)
C2	0.1411 (4)	0.2653 (3)	0.1002 (6)	0.036 (2)
C3	0.2897 (5)	0.2846 (3)	0.4571 (6)	0.040 (2)
C4	0.1914 (5)	0.3862 (3)	0.0833 (6)	0.044 (2)
N1	0.3778 (5)	0.3346 (3)	0.5941 (5)	0.057 (2)
N2	0.2323 (5)	0.4817 (3)	0.0721 (6)	0.071 (2)
C15	0.3027 (5)	−0.1625 (3)	−0.3632 (6)	0.050 (2)
C14	0.3769 (5)	−0.0587 (3)	−0.2596 (6)	0.047 (2)
C13	0.4589 (4)	−0.0555 (3)	−0.0567 (6)	0.035 (2)
C12	0.4610 (5)	−0.1619 (3)	0.0359 (6)	0.047 (2)
C11	0.3841 (6)	−0.2639 (3)	−0.0727 (7)	0.052 (2)
N10	0.3084 (4)	−0.2634 (3)	−0.2704 (5)	0.044 (2)
C5	0.2332 (6)	−0.3746 (3)	−0.3915 (8)	0.064 (3)

Table 2. *Geometric parameters* (Å, °)

Pd1—S1	2.290 (1)	C1—C3	1.429 (5)
Pd1—S2	2.304 (1)	C2—C4	1.438 (5)
S1—C1	1.731 (3)	C3—N1	1.147 (5)
S2—C2	1.727 (3)	C4—N2	1.136 (5)
C1—C2	1.377 (5)		
S1—Pd1—S2	90.0 (1)	S1—C1—C2	122.8 (2)
S1—Pd1—S1*a*	180.0 (1)	S1—C1—C3	116.1 (3)
S2—Pd1—S1*a*	90.0 (1)	C2—C1—C3	121.0 (3)
S1—Pd1—S2*a*	90.0 (1)	S2—C2—C1	122.8 (2)
S2—Pd1—S2*a*	180.0 (1)	S2—C2—C4	118.2 (3)
S1*a*—Pd1—S2*a*	90.0 (1)	C1—C2—C4	119.0 (3)
Pd1—S1—C1	102.3 (1)	C1—C3—N1	177.2 (4)
Pd1—S2—C2	102.1 (1)	C2—C4—N2	179.2 (4)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71213 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1047]

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The Optical Resolution of Bicyclo[2.2.1]-hept-5-ene-2-cyanohydrins Using Brucine – a Crystallographic and Molecular-Mechanics Study

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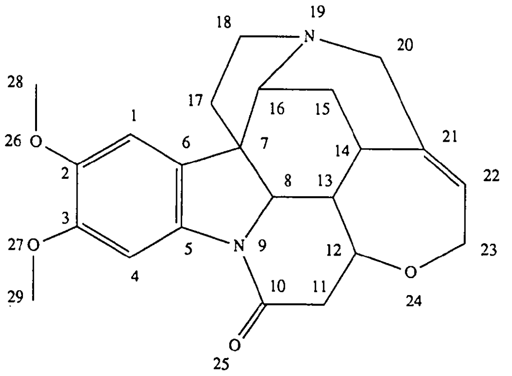
Abstract

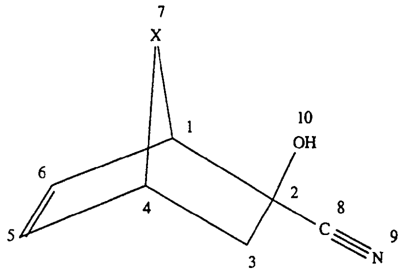
The structures of the brucine complexes with (+)-(1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-cyanohydrin and (+)-(1*R*,2*R*,4*R*)-7-oxabicyclo[2.2.1]hept-5-ene-2-cyanohydrin {(6) 2,3-dimethoxystrychnidine-2-hydroxybicyclo[2.2.1]hept-5-ene-2-carbonitrile (1/1) and (7) 2,3-dimethoxystrychnidine-2-hydroxy-7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile (1/1)} have been determined. The primary interaction in the complexes is a hydrogen bond between the OH group of the cyanohydrin and the most basic N atom of brucine. Molecular-mechanics calculations on the 7-oxa derivative indicate that the enantiomeric cyanohydrin will fit into the same cavity in the brucine matrix at the cost of *ca* 71 kJ mol^{-1}.

Comment

There is current interest in understanding the mechanism of molecular recognition (Schneider, 1991) and in the resolution of racemic mixtures. The use of naturally occurring optically pure bases to form diastereomeric salts of differing solubility from racemic acids has been employed for over a century (Pasteur, 1853). More recently, brucine (1) was used to resolve some tertiary acetylenic alcohols by fractional crystallization of the diastereomeric complexes. For one of the complexes, the primary interaction was shown to be formation of a hydrogen bond between the OH group of the alcohol and N19 of brucine (Toda, Tanaka & Ueda, 1981; Toda, Tanaka, Ueda & Oshima, 1985). Applying this technique to the cyanohydrin mixture, (2)/(3), formed by (±)-bicyclo[2.2.1]hept-5-en-2-one (4) and (±)-7-oxabicyclo[2.2.1]hept-5-en-2-one (5), we have been able to prepare optically pure (+)-(4) and (+)-(5), and also to use the resolved brucine/cyanohydrin complexes directly as synthons for the preparation of natural compounds (Black & Vogel, 1984; Warm & Vogel, 1986*a*,*b*, 1987; Vogel, Fattori, Gasparini & LeDrian, 1990; LeDrian & Greene, 1982). We have thus determined the structures of the brucine complexes (6) and (7) of the cyanohydrins derived from (+)-(4) and (+)-(5) to investigate the nature of the interaction in the complex and to gain insight into the determining factors in optical



(1)



(2) $X = CH_2$
(3) $X = O$

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